Doubly Doped Lithium Niobate Crystals

TECHNICAL FIELD

The invention relates to the field of photorefractive crystal material.

BACKGROUND ART

Three-dimensional optical storage will enter the market, but it does not mean that the product has been done very well. The main problem is no excellent three-dimensional optical storage material found. In fact, scientists in the world have been looking for satisfied three-dimensional optical storage material for a long time. Up to now, the iron doped lithium niobate is still considered as the first candidate. But there are big shortcomings for $LiNbO_3$: Fe, such as a too long response time and a low ability to resist optic scattering (A. Hellemans, Holograms can storage terabytes, but where? Science 286 (1999) 1502). Now, improving and optimizing the properties of $LiNbO_3$: Fe crystal (restrain the laser induced voltage effect and maintain its good photorefraction properties in the mean time) is still the most important task at present.

DISCLOSURE OF THE INVENTION

The objection of this invention is to supply a doubly doped lithium niobate crystal, which is an improvement and optimization of $LiNbO_3$: Fe, and has an excellent photorefractive properties, and can be used as the three-dimensional holographic optical storage material.

The doubly doped lithium niobate crystal of the invention is doped with iron and a second radius-matched metal ion in the meantime. Its composition can be denoted as $Li_{1-x}Nb_{1+y}O_3$: Fe_m,M_n, where M is magnesium, indium, or zinc; when using q to denote the ion valence of M (q=2 when M is Mg or Zn, and q=3 when M is In), the values of x, y, m, and n are in the range of $0.05 \leq x \leq 0.13$, $0.00 \leq y \leq 0.01$,

$5.0\times10^{-5}\leq m\leq7.5\times10^{-4}$, and $0.02\leq qn\leq0.13$, respectively.

The composition of doubly doped lithium niobate crystals can :

doped with 0.007~0.03 wt.% Fe and 1.0~5.0 mol.% Mg,

doped with 0.01~0.05 wt.% Fe and 0.75~3.0 mol.% In, or

doped with 0.02~0.06 wt.% Fe and 1.5~6.5 mol.% Zn,

While the congruent composition is [Li]/[Nb]=0.87~0.95.

The implement steps of the invention are:

(1) Weigh up Li_2CO_3, Nb_2O_5, Fe_2O_3, and MgO, In_2O_3 or ZnO powders according to the crystal composition, and dry them at 120~150°C for 2~5 hours, then thoroughly mix them at a mixer lasting for 24 hours, and keep them at 800~850°C for 2~5 hours to make Li_2CO_3 decompose sufficiently, and then sinter at 1050~1150°C for 2~8 hours to obtain doubly doped lithium niobate powder. (2) Put the above doped lithium niobate powder into a Pt crucible after impacted then heat the powder by a middle frequency stove. Grow the doubly doped lithium niobate crystals using the Czochralski pulling method along c or a axis via the procedures of necking, shouldering, uniform-diametering, and tailing, with the pulling rate being 1~3 mm/h, the rotation rate being 15~30 rpm, the temperature difference of the melt-crystal interface being 20°C, the temperature gradient in the melt volume near the surface being 1.5°C/mm, and the temperature gradient above the melt surface being 1.0°C/mm, respectively. (3) Pole and anneal the grown doped lithium niobate crystals at 1200°C to obtain a single-domain structure.

OPTIMUM REALIZATION OF THE INVENTION

The outstandingly essential characteristics and effects of the invention can be seen from the following embodiments, but they do no limit to the scope of this invention.

Embodiment 1:

(1) Weigh up 0.01 wt.% Fe_2O_3 and 3 mol.% MgO, and

$[Li_2CO_3]/[Nb_2O_5]=0.94$. and dry them at 150°C for 2 hours, then thoroughly mix them at a mixer lasting for 24 hours, and keep them at 850°C for 2 hours to make Li_2CO_3 decompose sufficiently, and then sinter at 1100°C for 2 hours to obtain doubly doped lithium niobate powder. (2) Put the above doped lithium niobate powder into a Pt crucible after impacted then heat the powder by a middle frequency stove. Grow the doubly doped lithium niobate crystals using the Czochralski pulling method along c axis via the procedures of necking, shouldering, uniform-diametering, and tailing, with the pulling rate being 3 mm/h, the rotation rate being 27 rpm, the temperature difference of the melt-crystal interface being 20°C, the temperature gradient in the melt volume near the surface being 1.5°C/mm, and the temperature gradient above the melt surface being 1.0°C/mm, respectively. (3) Pole and anneal the grown doped lithium niobate crystals at 1200°C to get a single-domain structure. After being orientated, cut, grinded, and polished to optical grade, the maximum diffraction efficiency of this Fe and Mg doubly lithium niobate crystal is 70%, the light intensity threshold to optic scattering is larger than 20 mW, and the average write time for holographic storage is 5 s ($I \sim 1\ W/cm^2$).

Embodiment 2:

(1) Weigh up 0.015 wt.% Fe_2O_3 and 0.5 mol.% In_2O_3, and $[Li_2CO_3]/[Nb_2O_5]=$ 0.945. and dry them at 150^0C for 2 hours, then thoroughly mix them at a mixer lasting for 24 hours, and keep them at 850°C for 2 hours to make Li_2CO_3 decompose sufficiently, and then sinter at 1100°C for 2 hours to obtain doubly doped lithium niobate powder. (2) Put the above doped lithium niobate powder into a Pt crucible after impacted , then heat the powder by a middle frequency stove. Grow the doubly doped lithium niobate crystals using the Czochralski pulling method along c axis via the procedures of necking, shouldering, uniform-diametering, and tailing, with the pulling rate being 2 mm/h, the rotation rate being 25 rpm, the temperature difference of the melt-crystal interface being

20°C, the temperature gradient in the melt volume near the surface being 1.5°C/mm, and the temperature gradient above the melt surface being 1.0°C/mm, respectively. (3) Pole and anneal the grown doped lithium niobate crystals at 1200°C to get a single-domain structure. After being orientated, cut, grinded, and polished to optical grade, the maximum diffraction efficiency of this Fe and In doubly lithium niobate crystal is 72%, the light intensity threshold to optic scattering is larger than 30 mW, and the average write time for holographic storage is 3 s (I~1 W/cm^2).

Embodiment 3:

(1) Weigh up 0.025 wt.% Fe_2O_3 and 6 mol.% ZnO, and $[Li_2CO_3]/[Nb_2O_5]=0.88$. and dry them at 150°C for 2 hours, then thoroughly mix them at a mixer lasting for 24 hours, and keep them at 850°C for 2 hours to make Li_2CO_3 decompose sufficiently, and then sinter at 1100°C for 2 hours to obtain doubly doped lithium niobate powder. (2) Put the above doped lithium niobate powder into a Pt crucible after impacted, then heat the powder by a middle frequency stove. Grow the doubly doped lithium niobate crystals using the Czochralski pulling method along c axis via the procedures of necking, shouldering, uniform-diametering, and tailing, with the pulling rate being 1.5 mm/h, the rotation rate being 20 rpm, the temperature difference of the melt-crystal interface being 20°C, the temperature gradient in the melt volume near the surface being 1.5°C/mm, and the temperature gradient above the melt surface being 1.0°C/mm, respectively. (3) Pole and anneal the grown doped lithium niobate crystals at 1200°C to get a single-domain structure. After being orientated, cut, grinded, and polished to optical grade, the maximum diffraction efficiency of this Fe and Zn doubly lithium niobate crystal is 68%, the light intensity threshold to optic scattering is larger than 50 mW, and the average write time for holographic storage is 3 s (I~1 W/cm^2).

INDUSTRIAL APPLICABILITY

The invented doubly doped lithium niobate crystals have high diffraction efficiency for three-dimensional holographic photorefractive grating, which is more than 68 %. The photorefractive response time is 3~5 s, an order of magnitude faster than LiNbO3: Fe. They have a high resistance to optical scattering, that is the light intensity threshold for photorefractive fanning optical scattering is as almost two orders of magnitude higher than $LiNbO_3$: Fe crystal. Comparing with the same products in the world, the response times of these doubly doped lithium niobate crystals have been improved by 1-2 orders of magnitude so as to be an excellent three-dimensional holographic optical storage material. These doubly doped lithium niobate crystals have widely potential applications in three-dimensional holographic optical disk, integration optics, military antagonizing, civil navigation, finance, stocks, etc.